4101-130-55X

TITLE OF THE INVENTION

FE-CO-NI ALLOY AND USE FOR THE MANUFACTURE OF A SHADOW MASK

Field of the invention

The present invention relates to an Fe-Ni-Co alloy having a low coefficient of expansion, as well as to its use in the manufacture of a shadow mask for, e.g., a display cathode ray tube.

Discussion of the Background

Certain Fe-Ni-Co alloys having a low coefficient of expansion, commonly called SUPERINVAR, are known in the art. These alloys are used especially for the manufacture of shadow masks as described, for example, in European Patent Application EP 0534460 which proposes to use, for the manufacture of shadow masks, an Fe-Ni-Co alloy containing, by weight, in addition to iron, from 28% to 34% of nickel, from 2% to 7% of cobalt, from 0.1% to 1% of manganese, less than 0.1% of silicon and less than 0.01% of carbon, the rest being impurities resulting from smelting. However, this alloy has the drawback of sometimes having a martensitic transformation start point M_s close to room temperature so that, either when forming the shadow mask or when storing it at low temperature, the martensitic transformation starts, causing permanent deformation of the shadow mask. In addition, especially because of the manganese content, which is regarded as being necessary for the alloy to exhibit good hot-rolling behaviour, the alloy has a coefficient of expansion which is too high to

sufficiently reduce the defect of local doming of the shadow mask.

SUMMARY OF THE INVENTION

One object of the present invention is to provide an Fe-Ni-Co alloy which has a martensitic transformation start point of less than -50°C, an average coefficient of thermal expansion between 20°C and 100°C of less than or equal to $0.7\times10^{-6}/°K$ and a mean coefficient of thermal expansion between 80°C and 130°C of less than or equal to $1\times10^{-6}/°K$. Another object is the provision of shadow masks comprising this alloy. Other objects will become apparent upon an appreciation of the entire invention.

These objects are provided by an Fe-Ni-Co alloy whose chemical composition comprises, by weight based on total weight:

$$32\% \leq Ni \leq 34\%$$

$$3.5\% \leq Co \leq 6.5\%$$

$$0\% \leq Mn \leq 0.1\%$$

$$0\% \leq Si \leq 0.1\%$$

$$0\% \leq Cr \leq 0.1\%$$

$$0.005\% \leq C \leq 0.02\%$$

$$S \leq 0.001\%$$

$$0.0001\% \leq Ca \leq 0.002\%$$

$$0.0001\% \leq Mg \leq 0.002\%$$

the substantial remainder (at least 50%, preferably at least 55%) being iron and impurities resulting from smelting; the

chemical composition of the alloy furthermore satisfying the relationships:

$$Co + Ni \leq 38.5\%$$

$$Co + 0.5 \times Ni \geq 20\%$$

$$Co + 5 \times Ni \geq 165.5\%$$

and

$$S \leq 0.02 \times Mn + 0.8 \times Ca + 0.6 \times Mg$$

Preferably, the copper, molybdenum, vanadium and niobium contents are each less than 0.1 wt%. Even better, the sum of the manganese, silicon, chromium, copper, molybdenum, vanadium and niobium contents is less than 0.30 wt%.

Additionally, it is preferable that the oxygen content be less than or equal to 0.01 wt%, and/or the nitrogen content be less than or equal to 0.005 wt% and/or the phosphorus content be less than or equal to 0.005 wt%.

The use of the above alloy according to the invention for the manufacture of a shadow mask, as well as the shadow mask thus obtained, are also part of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Although it is generally known and accepted that the deformations of a shadow mask are principally generated by moderate heating up to a temperature of less than 100°C and typically a temperature of 80°C, the inventors believe, based on their study, that image defects are caused by local heating of the shadow mask at temperatures which might be as high as 130°C. In order to reduce image defects as far as possible,

the inventors discovered that it is necessary to use, for the manufacture of a shadow mask, an alloy which not only has a mean coefficient of expansion between 20°C and 100°C which is low, preferably as low as possible, but which also has a mean coefficient of expansion between 80°C and 130°C which is low, again preferably as low as possible. In addition, this alloy should have a micrographic structure which is stable down to a sufficiently low temperature, that is to say down to at least -50°C.

The alloy according to the invention satisfying the above objects is an Fe-Ni-Co alloy whose chemical composition is adjusted so that, simultaneously, its mean coefficient of expansion between 20°C and 100°C is less than or equal to 0.7×10^{-6}/°K, its mean coefficient of expansion between 80°C and 130°C is less than or equal to 1×10^{-6}/°K and its M_s point is less than -50°C.

The chemical composition of the invention alloy preferably comprises, by weight based on total weight, at least 32% and at most 34% of nickel, as well as at least 3.5% and at most 6.5% of cobalt, the nickel and cobalt contents being such that:

$$Co + Ni \leq 38.5\%$$

so that, it is believed, the mean coefficient of expansion of the alloy between 20°C and 100°C is less than or equal to 0.7×10^{-6}/°K;

$$Co + 0.5 \times Ni \geq 20\%$$

so that, it is believed, the mean coefficient of expansion between 80°C and 130°C is less than $1\times10^{-6}/°K$;

$$Co + 5 \times Ni \geq 165.5\%$$

so that, it is believed, the M_s point is less than -50°C.

It is also believed that in order for the mean coefficient of expansion between 20°C and 100°C to be less than or equal to $0.7\times10^{-6}/°K$, it is preferable for each of the manganese, silicon and chromium contents to be less than or equal to 0.1%.

In order for the M_s point to remain below -50°C, it is believed that the alloy should contain at least 0.005% of carbon; however, the carbon content should not exceed 0.02% so that there is no deterioration in the ability to be shaped by drawing.

However, industrial alloys always contain residual elements such as copper, molybdenum, vanadium or niobium, and, in order for the coefficient of expansion to be as low as possible, it is desirable for the contents of each of these elements to remain less than or equal to 0.1% and, preferably, for:

$$Mn + Si + Cr + Mo + V + Nb + Cu \leq 0.30\%.$$

Finally, in order to obtain better hot ductility, it is preferable for the oxygen content to be less than or equal to 0.01%, and/or the nitrogen content to remain less than or equal to 0.005%, and/or the phosphorus content to remain less than or equal to 0.005%.

With this invention alloy, it is possible to manufacture shadow masks. For one way to do this, the alloy is smelted, cast as an ingot or slab and then hot-rolled in order to form a strip approximately 4 mm thick; the strip is then cold-rolled in order to obtain a cold-rolled strip approximately 0.15 mm thick. This cold-rolled strip has a 0.2% proof stress $R_{p0.2}$ at 20°C of about 600 MPa, which is much too high for allowing easy shaping, and in addition, after machining the mask blanks by chemical cutting, these blanks are subjected to an annealing between 700°C and 850°C which brings the 0.2% proof stress $R_{p0.2}$ at 20°C back down to about 320 MPa. Next, each blank is shaped, for example by drawing, in order to obtain a shadow mask.

EXAMPLES

By way of nonlimiting example, alloys A to D according to the invention were manufactured, the chemical compositions of which were, in % by weight based on total weight:

Ref	Ni	Co	Mn	Si	Cr	C	S	Ca	Mg	Fe
A	32.7	4.5	0.06	0.08	0.04	0.014	0.0006	0.0005	0.0015	bal.
B	33.5	4.5	0.05	0.08	0.07	0.014	0.0009	0.0012	0.0009	bal.
C	33.5	3.5	0.05	0.08	0.05	0.011	0.0007	0.0008	0.0007	bal.
D	33.3	4.2	0.05	0.09	0.06	0.018	0.0008	0.0011	0.0011	bal.

The properties of these alloys were:

Ref	α 20°/100° 10^{-6}/°K	α 20°/80° 10^{-6}/°K	α 80°/130° 10^{-6}/°K	M_s °C	$R_{p0.2}$ MPa 20°C work-hardened	$R_{p0.2}$ MPa 20°C annealed*	$R_{p0.2}$ MPa 200°C annealed*
A	0.31	0.23	0.78	-90	615	320	141
B	0.65	0.65	0.80	<-186	615	318	137
C	0.49	0.45	0.90	<-186	607	304	133
D	0.51	0.49	0.77	<-186	629	322	148

* 15 minute 780°C anneal

With these alloys, shadow masks were made consisting, in particular, of a foil drilled with holes and shaped by drawing. These shadow masks had an entirely austenitic structure, even after shaping or after storing in a cold environment, and their local doming defect is less than 40% of the local doming defect of shadow masks made of iron-nickel alloy according to the prior art.

This application is based on French patent application 95 05362 filed May 5, 1995, incorporated herein by reference.